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Spectroscopy studies on conductive polyaniline – polyimide blend films

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ABSTRACT

Conducting films of ± 10 camphorsulfonic acid (CSA)-doped polyaniline / polyimide (PANI/PI) blends with various compositions were prepared by solvent casting process. The molecular level interaction in these blend films were experimentally characterized by Fourier transform infrared (FTIR), Raman, UV-Vis and X-ray diffraction (XRD) spectroscopic techniques. The interacting structure and observed red shift confirm the presence of hydrogen bonding between the carbonyl group of PI with the amine of PANI that affects the optical band gap (E_g), electrical conductivity (σ) as well as the morphology of the blends. The disappearance of the characteristic peaks of PANI-CSA after blends with PI suggests some kind of molecular mixing between the two components and compatibility between the conducting and non-conducting polymers.

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Introduction

Polymer blends are a key component of current polymer research and technology, owing to their ease in production of new materials by mixing and in the diversity of their properties that result. Polyaniline (PANI) is an attractive conducting polymer since last decade due to its considerable conductivity, easy synthesis route and good thermal stability. However, the conducting forms of PANI are inherently brittle and poor in processability [1, 2]. A way of overcoming this problem is to prepare blends of PANI with conventional polymers, such as polyvinylchloride [3], nylons [4], and poly (methyl methacrylate) [5] or with high performance polymers such as polyimide, polysulfone and poly (amide imide) [6, 7] to maintain the mechanical properties, the processability, and the thermal stability of conventional or high performance polymers, together with the electrical properties of conducting polyaniline.

Aromatic polyimides (PI) show outstanding thermal, mechanical, electrical and solvent resistance properties that have been widely used as the high performance parts in electronic, aerospace and automobile industries [8]. Many reports are available on the preparation and characterization of conductive blends of PANI / PI by the conversion process of PANI / polyamic acid that involves some kind of critical processing conditions [9-13]. The characteristics of this type of blend are different from the "mixed conducting polymers", which are merely a physical mixture of non-conductive polymer with conducting polymer. It is imperative to understand the behaviour and molecular interactions in such mixed polymers will throw some light on the relationship between structures and properties as well as to predict properties or even to design new materials with specific characteristics. The objectives of this study are to report on the investigation of the molecular interactions in PANI / PI blend films using Fourier infra-red (FTIR) and Raman

spectroscopic techniques. The blend films were also examined by ultraviolet-visible (UV-Vis) spectroscopy to probe the nature of transition and to determine the optical band gap. We have also reported our observations of the electrical conductivity and structural analysis of PANI / PI blend films.

Experiment

Chemicals and Preparation of Polyaniline-Polyimide (PANI / PI) Blend films

Aniline (synthetic grade from Aldrich) was purified by distillation before use and ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), HCl and NH_4OH were used as received for the synthesis of polyaniline emeraldine base. (\pm)-10-camphor sulfonic acid (Lancaster), m-cresol (Aldrich) and polyimide (Indian space research organization (ISRO), India) were also used as received to prepare conductive PANI / PI blend films. Polyaniline emeraldine base (PANI-EB) powder was prepared by conventional chemical method [14]. To prepare conductive PANI powder, PANI-EB and (\pm)-10-camphor sulfonic acid (CSA) powders were mixed in a molar ratio of 0.2 CSA to polymer repeat unit phenylnitrogen. (PANI)_x-(PI)_{1-x} polyblend solutions (2wt %) were prepared by mixing the conductive PANI with PI in the specified stoichiometric ratio ($x = 0, 25, 50, 75$ and 100 % wt) and stirred mechanically in the presence of m-cresol for about 24 hours at room temperature. The resulting polyblend solutions appeared to be very uniform with no visible un-dissolved portion, which was used for the preparation of PANI / PI blend films by solution casting technique [15].

Measurements

Infrared measurements in the range 400–2000 cm^{-1} were recorded with a fully computerized Bruker IFS - 66V spectrometer with 200 scans per spectrum at 2 cm^{-1} resolution. All the measurements were performed *ex situ* in the transmission mode as KBr tablets. The optical transmittance spectra were

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recorded from 300 to 800 nm wavelength using a Hitachi UV-Vis-NIR spectrophotometer (U-3400). Unpolarized radiation at room temperature with a resolution of 2 nm was used in this study. The measurements were made on films of typical thickness (10 μm) deposited on glass substrates. The substrate absorption is corrected by introducing an uncoated cleaned glass substrate in the reference beam. In the present study, room temperature X-ray diffraction patterns were recorded using Philips X-ray generator (Model PW 1390) with an Ni filter and $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 20 mA in the 2θ range of 10° to 70° with an accuracy of 0.02° . Thickness of the PANI film ($9.8 \times 10^{-6} \text{ m}$), employed in this investigation was measured using a universal length-measuring instrument (TRIMOS, Switzerland) to an accuracy of $\pm 0.1 \times 10^{-6} \text{ m}$ (the pressure maintained in the ball contact was 2.47 Pa) and confirmed with alpha step surface profilometer (TENCOR Alpha step 200-ALO2). The area of the film, used for the conduction study was $\sim 5 \times 10^{-6} \text{ m}^2$, as measured using a profile projector (Nikon-V-20A, Japan) with 10 times magnification. For conduction measurements, Metal-Polyaniline-Metal (MPM) sandwich devices were prepared by evaporating gold in a vacuum of $2.7 \times 10^{-3} \text{ Pa}$ onto well-cleaned glass substrates through suitable masks to form bottom and top electrodes. The dc conductivity data was acquired using a constant current source coupled with a high-input impedance electrometer (Lab Equip. India). For all conductivity data presented here, the sample container was pumped for few hours before the data acquisition, to eliminate the effects of any absorbed moisture.

Results and discussion

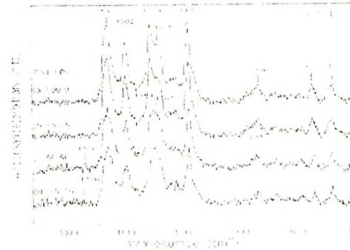
Experimental Study

Infra Red spectra

The FTIR spectra of PANI (a), PANI / PI blends with the weight ratio of 75:25 (b), 50:50 (c) and 25:75 (d) are shown in Fig.1. The IR main peaks of PANI and PI are identified. The PANI shows quinoid (Q) ring stretching at 1597 cm^{-1} , and benzenoid (B) ring stretching at 1502 cm^{-1} typical feature of a semiquinoid structure of emeraldine type [16]. The bands at 1371 cm^{-1} and 1345 cm^{-1} corresponds to B-N=Q and C_{ar} -N stretching modes respectively. The absorption peaks at 1175 cm^{-1} and 804 cm^{-1} are due to C-H in plane and out of plane bending vibrations of the aromatic ring respectively. The IR and Raman peaks of PANI / PI blend (b) peaks are similar to conductive PANI. In the case of (c) and (d) the carbonyl C=O stretching band of PI seen at 1730 cm^{-1} (d) shifts to 1720 cm^{-1} (c) as the PANI content increases from 25% to 50% wt. As the content of PANI increases, the carbonyl band becomes smaller and its peak shows a broad band. The observed red shift is due to the formation of hydrogen bond between the C=O group of PI with the amine of PANI, without allowing the amine to participate in protonation (Scheme1). A similar observation has been reported for thermally imidized PANI / polyamic acid (PAA) blends [13]. Since O is highly electronegative the hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the stretching force constant, which results in a lowering of the absorption frequency. The hydrogen bond between the C=O group of PI with the amine of PANI also affects the B-N=Q stretching mode. Because of this reason the band at 1371 cm^{-1} (a) shift to 1354 cm^{-1} (c). The band at 1336 cm^{-1} is assigned to the characteristic band of C_{ar} -N stretching (a) indicate the doped state of PANI. This band almost disappears in the case of (d) due to the availability of more carbonyl group

of PI that hampers the protonation. This fact is also seen as the intensity of the band at 1502 cm^{-1} decays where the band C-NH⁺=C turns into C-N=C characterizes the deprotonated structure.

Fig. 1 FT-IR spectra of PANI, PANI/PI blend films.

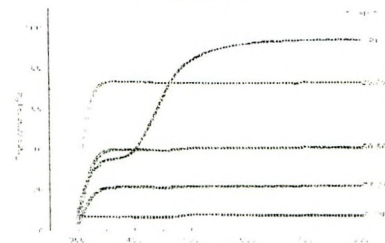


Optical spectra

The transmittance (T) data of polyaniline (PANI), polyimide (PI) and PANI / PI blend films (Fig.2) show the higher transmission in the higher wavelength region and its decline at absorption edge. Analysis of the absorption coefficient (α) has been carried out to determine the nature of transitions involved and to obtain the optical band gap (E_g). Absorption coefficient data were elucidated from optical transmission measurements in the interference-free, strong absorption spectral region. The frequency dependence of the absorption coefficient can be described by an empirical relation.

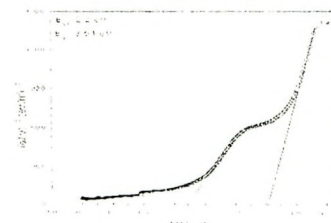
$$\alpha h\nu = A(h\nu - E_g)^n$$

Fig. 2 Transmittance spectra of PANI, PI and PANI/PI blend films.

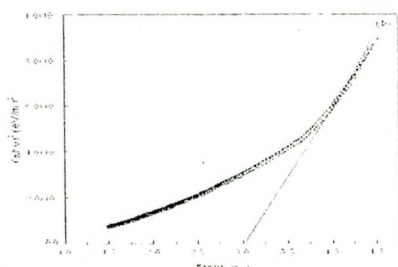


where A is a material constant. E_g a characteristic energy termed as optical band gap and n is the transition probability index, which has discrete values like $1/2$, $3/2$, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden. The plots of $(\alpha h\nu)^2$ versus $h\nu$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$ are linear function, indicating the existence of direct allowed and indirect allowed transition in PANI and PI, PANI / PI blends respectively. Extrapolation of linear dependence of the relation to abscissa yields the corresponding bandwidth E_g . The values of the optical energy gaps obtained from Fig. 3 (a), (b) and (c) are listed in Table 1.

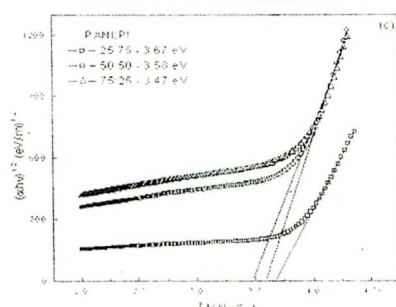
Fig. 3 (a) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ show indirect allowed transition in PI,



(b) Plot of $(\alpha h\nu)^2$ verses $h\nu$ show direct allowed transition in PANI



(c) Plot of $(\alpha h\nu)^{1/2}$ verses $h\nu$ show indirect allowed transition in PANI / PI blend films.



From the table, it is observed that the percentage of transmittance (T) decreases with the increase of PANI concentration. At the same time the range of transparency almost remains same in PANI and its blends except for the polyimide film. The band gap evaluated for PANI (3 eV) almost matches with the reported result [17]. The band gap for PI film is calculated as 2.2, 3.51 eV. Yoo et al. [18] have recently reported the existence of only one optical band gap for polyimide (3.51 eV) matches with our result. However, there is an additional band gap (2.2 eV) obtained for PI film may be due to the formation of exciton. The exciton is a bound electron-hole pair, which can be formed in every insulating crystal, if the band gap is indirect. The exciton near the direct gap may be unstable with respect to decay into a free electron and free hole. The exciton also has different energy level. The energy of formation of an exciton is less than the band gap and so its energy level lies in the band gap. The optical band gap of the polyaniline blends shifts from 3.67 to 3.47 eV (bathochromic shift) when the PANI load (x) increases from 0.25 to 0.75. This bathochromic shift indicates the formation of hydrogen bonding between PI and PANI, which may result in weakening of bond strength in PANI. Similar results were reported for PANI - poly (vinyl alcohol) (PVA) and PANI - nylon 6 composites [4].

Structural and electrical conductivity

X-ray diffraction patterns of PANI, PI and PANI / PI blend films with the weight ratio of 75:25, 50:50 and 25:75 are shown in Fig.4. The CSA-doped PANI film has a prominent diffraction peaks at $2\theta = 18.7^\circ$ and 31.8° in the background of amorphous shoulder around 25° , indicating that some part of the PANI sub chains become rigid and ordered. A model for the structure of CSA doped polyaniline film explains the presence of alternating layers of flat emeraldine salt chains and CSA anion parallel (a,c) planes [19] grown parallel to the c axis. Here, polyaniline could be treated as a polycation while CSA acts as an anion that allows an increase in interchain packing and thus induces higher structural order. On the contrary, there are no pronounced

diffraction peaks in the patterns of PANI / PI blends indicating the synergetic effect of the presence of large number of hydrogen bonding moieties (C=O group of PI and amine of PANI) in polyblend films reducing the interchain packing and hence resulting in the conformational hindrance of PANI sub chain. The disappearance of the characteristic peaks also suggests some kind of molecular mixing between two components [13]. However, the improvement of electrical conductivity from 10^{-8} to 10^{-5} S/cm in this blend films as shown in the Table(1) is due the enrichment of the conducting path in the amorphous regions of PANI / PI blends that reduces the tunnelling/hopping distance between disordered regions results in the enhancement charge carrier motion.

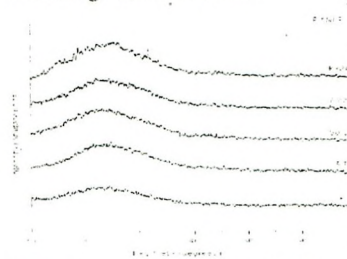
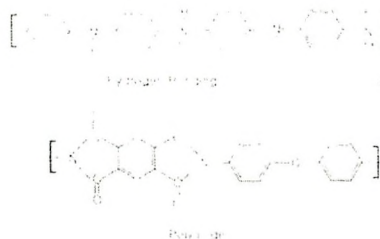


Fig. 4 X-ray diffraction patterns of PANI, PI and PANI-PI blend films.



Scheme 1 Kannusamy et al.

Conclusion

Conductive films of PANI / PI blends with different compositions were prepared by solvent casting process. The molecular level interaction in these blend films was experimentally characterized by Fourier transform infrared (FTIR), UV-Vis and X-ray diffraction (XRD) spectroscopic techniques. It was demonstrated that PANI can react with PI to form chemical bonds and keep them as a miscible system. The interaction between O of the carbonyl group in PI and H of amine in PANI hampers the protonation of latter, in turn increasing its band gap. The race between the dopant moieties and hydrogen bond moieties affect protonation process in the PANI / PI blend system which in turn influence the structural, optical and electrical properties. Theoretical study on structure and interacting nature of PANI/PI blends is in progress using density functional theory (DFT) and frontier molecular orbitals (FMO) for our future work.

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Table 1. Optical parameters of PANI, PI and PANI / PI blend films.

| Concentration PANI-PI (w/w)% | Type of transition | Band gap (E_g) | Percentage of transmittance | Range of transparency (nm) | Conductivity (S/cm) |
|------------------------------|--------------------|--------------------|-----------------------------|----------------------------|-----------------------|
| 0:100 (PI) | Indirect allowed | 2.2 and 3.51 | 94 | 550-800 | 5.43×10^{-9} |
| 25:75 | Indirect allowed | 3.67 | 72 | 350-800 | 1.54×10^{-8} |
| 50:50 | Indirect allowed | 3.58 | 41 | 360-800 | 3.14×10^{-7} |
| 75:25 | Indirect allowed | 3.47 | 22 | 360-800 | 2.38×10^{-5} |
| 100:0 (PANI) | Direct allowed | 3.0 | 7.5 | 330-800 | 7.82×10^{-5} |

Table 2 Assignments of main peaks of PANI-PI blend spectra (wave number in cm^{-1}).

| Peak assignment ^a | FT-IR |
|----------------------------------|-------|
| C=O (PI) | 1720 |
| C=C (Q ring of PANI) | 1597 |
| C-N=C (N-B-N of PANI) | 1502 |
| C-C Stretching of Q ring of PANI | 1354 |
| C _{sp} -N (PANI) | 1345 |
| C-H (in plane mode of PANI) | 1175 |
| C-H (out of plane mode of PANI) | 817 |

^aPANI-polyaniline, PI-polyimide, B=benzene ring, Q=quinoid ring.
Experimental values of IR and Raman are presented for 50:50% wt. of PANI-PI.